

On the Use of Linearized Langmuir Equations

Carl H. Bolster*

USDA-ARS
230 Bennett Ln.
Bowling Green, KY 42104

George M. Hornberger

Dep. of Environmental Sciences
Univ. of Virginia
Charlottesville, VA 22903

One of the most commonly used models for describing solute sorption to soils is the Langmuir model. Because the Langmuir model is nonlinear, fitting the model to sorption data requires that the model be solved iteratively using an optimization program. To avoid the use of optimization programs, a linearized version of the Langmuir model is often used so that model parameters can be obtained by linear regression. Although the linear and nonlinear Langmuir equations are mathematically equivalent, there are several limitations to using linearized Langmuir equations. We examined the limitations of using linearized Langmuir equations by fitting P sorption data collected on eight different soils with four linearized versions of the Langmuir equation and comparing goodness-of-fit measures and fitted parameter values with those obtained with the nonlinear Langmuir equation. We then fit the sorption data with two modified versions of the Langmuir model and assessed whether the fits were statistically superior to the original Langmuir equation. Our results demonstrate that the use of linearized Langmuir equations needlessly limits the ability to model sorption data with good accuracy. To encourage the testing of additional nonlinear sorption models, we have made available an easily used Microsoft Excel spreadsheet (ars.usda.gov/msa/awmru/bolster/Sorption_spreadsheets) capable of generating best-fit parameters and their standard errors and confidence intervals, correlations between fitted parameters, and goodness-of-fit measures. The results of our study should promote more critical evaluation of model fits to sorption data and encourage the testing of more sophisticated sorption models.

Abbreviations: AIC, Akaike's Information Criterion; SSE, sum of squared errors.

The transport behavior of environmentally significant reactive solutes such as P and heavy metals is controlled in large part by the sorption behavior of these solutes to soil surfaces. Sorption behavior to soils is often determined by measuring sorption isotherms, where a known mass of soil is equilibrated with a solution of known concentration of the solute of interest. After equilibration, the concentration remaining in solution is measured and used to calculate the concentration sorbed to the soil (Nair et al., 1984). A sorption model is fit to the data to obtain sorption parameters for the soil. These sorption parameters are used to estimate parameters such as the sorption capacity of the soil or retardation coefficients to be used in transport modeling. The accuracy of the model parameters will depend on whether the appropriate conceptual model was chosen, whether the experimental conditions were representative of environmental conditions, and whether an appropriate parameter estimation method was used.

A commonly used model for describing sorption behavior is the Langmuir model (Altin et al., 1998; Kumar and Sivasan, 2005; Kleinman and Sharpley, 2002; Tsai and Juang, 2000; Wang and Harrell, 2005). Because the Langmuir model is non-

linear, fitting this model to measured data requires a "trial and error" approach. That is, values of the parameters are inserted into the model, the sorbed concentrations are calculated with the model, the model-calculated values are then compared with the observed data, the model parameters are adjusted, and the process is repeated until the best agreement between modeled and observed data is achieved. Alternatively, a linearized version of the Langmuir equation—at least four different versions exist (Table 1)—can be used so that the model parameters can be obtained directly by solving the normal equations (i.e., by linear regression). Because linear regression is convenient, requires little understanding of the data-fitting process, and is easily done in spreadsheets such as Microsoft Excel, this method is commonly used for obtaining Langmuir sorption parameters (Borling et al., 2001; D'Angelo et al., 2003; Fang et al., 2002; Kleinman and Sharpley, 2002; Sharpley, 1995; Siddique and Robinson, 2003; Xu et al., 2006; Zhang et al., 2005). A limitation to this approach, however, is that the transformation of data required for linearization can result in modifications of error structure, introduction of error into the independent variable, and alteration of the weight placed on each data point (Dowd and Riggs, 1965; Harter, 1984), often leading to differences in fitted parameter values between linear and nonlinear versions of the Langmuir model (Altin et al., 1998; Kumar and Sivasan, 2005; Schulthess and Dey, 1996; Tsai and Juang, 2000).

Although it is commonly assumed that linearized versions of the Langmuir model provide poorer fits and less accurate parameter estimates than the nonlinear equation (Harrison and Katti, 1990; Kumar and Sivasan, 2005; Kinniburgh, 1986), the most accurate Langmuir equation will depend on the error structure of the data because a major assumption in regression analyses is that the variance of the errors remains constant. Therefore, if a

Soil Sci. Soc. Am. J. 71:1796–1806

doi:10.2136/sssaj2006.0304

Received 30 Aug. 2006.

*Corresponding author (carl.bolster@ars.usda.gov).

© Soil Science Society of America

677 S. Segoe Rd. Madison WI 53711 USA

All rights reserved. No part of this periodical may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher.

Permission for printing and for reprinting the material contained herein has been obtained by the publisher.

transformation improves the constancy of the error variance, then the associated linear equation will provide better fits and more accurate parameter estimates than the nonlinear equation (Colquhoun, 1969). For example, while the nonlinear equation has been shown to provide the most accurate parameter estimates when the error variance remains constant (Atkins and Nimmo, 1975; Colquhoun, 1971; Gerringa et al., 1995; Persoff and Thomas, 1988), linearized versions of the Langmuir equation have been shown to provide slightly better parameter estimates than the nonlinear equation when the error variance increases linearly with the dependent variable (Atkins and Nimmo, 1975; Colquhoun, 1971).

An important limitation to these earlier studies, however, is that they have been conducted primarily on simulated data sets under conditions not necessarily representative of sorption studies. Even in studies that do compare fitted parameter values between linear and nonlinear Langmuir equations on measured sorption data, parameter uncertainties are rarely included so it is unknown whether the differences in fitted parameters between the different equations are statistically significant (Allen et al., 2004; Altin et al., 1998; Kumar and Sivanesan, 2005; Kinniburgh, 1986; Schulthess and Dey, 1996; Tsai and Juang, 2000). Therefore, the accuracy of the linearized Langmuir equations is still unclear. This is of particular importance in P sorption studies where linearized Langmuir equations are commonly used for obtaining soil sorption parameters (Borling et al., 2001; D'Angelo et al., 2003; Fang et al., 2002; Kleinman and Sharpley, 2002; Sharpley, 1995; Siddique and Robinson, 2003; Xu et al., 2006; Zhang et al., 2005).

While statistical differences between linear and nonlinear forms of the Langmuir model have been noted for some time (Colquhoun, 1969, 1971; Dowd and Riggs, 1965; Kinniburgh, 1986; Kumar and Sivanesan, 2005; Schulthess and Dey, 1996), of greater concern is whether the Langmuir model itself is the most appropriate model for describing the data. Sorption data often do not conform to the standard Langmuir plot (Giles et al., 1974; Grant et al., 1998; Gu et al., 1994; Holford et al., 1974; Kinniburgh, 1986; Sposito, 1982), yet this may not be apparent when viewing linearized model fits to transformed data (Harter, 1984). Furthermore, the ease with which linearized Langmuir equations can be fit to data may discourage critical evaluation of the model fits. This in turn can lead to accepting the fitted model parameters as representative of the soil when in fact the data do not conform to the Langmuir model at all. Instead, a modified version of the Langmuir model may be more appropriate for describing the data (Grant et al., 1998; Hinz, 2001). Because linearized versions of these modified equations do not exist, the largest drawback to relying on linear regression may not be statistical differences between linear and nonlinear forms of the Langmuir model, but rather the inability to test more sophisticated nonlinear sorption models that cannot be linearized.

In this study, we set out to further our understanding of the limitations of using linearized Langmuir equations. Such understanding is particularly important in P sorption studies, where linearized Langmuir equations are commonly used to obtain impor-

Table 1. Different linearized forms of the Langmuir equation. The commonly used name is in parentheses.

Equation	Equation form	Limitations
Linearization I (Hanes–Woolf)	$\frac{C}{S} = \frac{1}{S_{\max} K} + \frac{C}{S_{\max}}$	Because x (C) and y (C/S) are not independent, the correlation between x and y is overestimated, i.e., equation may provide good fits to data that do not conform to the Langmuir model.
Linearization II (Lineweaver–Burke)	$\frac{1}{S} = \frac{1}{S_{\max} K} \frac{1}{C} + \frac{1}{S_{\max}}$	Transformation leads to clumping of data points near origin—extremely sensitive to variability at low values of S (high values of $1/S$).
Linearization III (Eadie–Hofstee)	$S = S_{\max} - \frac{1}{K} \left(\frac{S}{C} \right)$	Abscissa is not error free; x (S/C) and y (S) data are not independent. In this case, correlation between x and y is underestimated, i.e., equation may provide poor fit to data that do conform to the Langmuir model.
Linearization IV (Scatchard)	$\frac{S}{C} = K S_{\max} - K S$	x (S) and y (S/C) are not independent. In this case, correlation between x and y is underestimated, i.e., equation may provide poor fit to data that do conform to the Langmuir model.

tant sorption parameters that are used in land management decisions. To investigate the limitations of parameter estimation for isotherms, we fit P sorption data collected on eight different soils with four linearized versions of the Langmuir equation and compared goodness-of-fit measures and fitted parameter values with those obtained with the nonlinear Langmuir equation. We then fit the sorption data with two modified versions of the Langmuir model and assessed whether the fits were statistically superior to the original Langmuir equation. Our results demonstrate that the reliance on linearized Langmuir equations potentially limits the ability to model sorption data accurately. Therefore, to encourage the testing of more sophisticated nonlinear sorption models, we have made available an accurate and easy-to-use Microsoft Excel spreadsheet capable of performing nonlinear regression. Results of this study will allow researchers to make more informed decisions when applying the Langmuir model to their sorption data.

MATERIALS AND METHODS

Sorption Data

Sorption isotherms were conducted on surface soil samples (0–15 cm) collected at seven locations in western Kentucky and one location in Alabama representing eight different soil series as follows: Belknap (coarse-silty, mixed, active, acid, mesic Fluvaquentic Endoaquepts), Collins (coarse-silty, mixed, active, acid, thermic Aquic Udifluvents), Hartsells (fine-loamy, siliceous, subactive, thermic Typic Hapludults), Lakin (mixed, mesic Lamellic Udipsamments), Loring (fine-silty, mixed, active, thermic Oxyaquic Fragiudalfs), Melvin (fine-silty, mixed, active, nonacid, mesic Fluvaquentic Endoaquepts), Pembroke (fine-silty, mixed, active, mesic Mollic Paleudalfs), and Zanesville (fine-silty, mixed, active, mesic Oxyaquic Fragiudalfs). Soils were air dried and passed through a 2-mm sieve before use. Soil samples (3 g) were equilibrated in 50-mL centrifuge tubes with 30 mL of a 0.01 mol L⁻¹ CaCl₂ solution containing either 5, 10, 15, 20, 30, or 40 mg L⁻¹ P added as KH₂PO₄ (Nair et al., 1984). The soil mixture was placed on a reciprocating shaker and allowed to equilibrate for 24 h. Following equilibration, the mixture was centrifuged at 4000 rpm for 10 min and the liquid decanted and filtered through a Whatman 0.45-μm filter. Dissolved reactive P was measured colorimetrically (Murphy and Riley, 1962) using a QuickChem Autoanalyzer (Lachat Instruments, Chicago, IL).

Data Analysis

Originally developed for describing the adsorption of gases to a surface (Langmuir, 1918), the Langmuir model is used extensively for describing solute and metal sorption to soils:

$$S = \frac{S_{\max} KC}{1 + KC} \quad [1]$$

where S is the sorbed concentration (mg kg^{-1}), S_{\max} is the maximum sorption capacity of the soil (mg kg^{-1}), K is the Langmuir binding-strength coefficient (L mg^{-1}), and C is the equilibrium concentration (mg L^{-1}). Equation [1] was fit to the sorption data and the fitted parameters and goodness-of-fit measures were then compared with those obtained from fitting the four linearized versions of Eq. [1] (Table 1) to the data using linear regression.

Because in many cases sorption data do not conform to the standard Langmuir plot (Giles et al., 1974; Grant et al., 1998; Gu et al., 1994; Holford et al., 1974; Kinniburgh, 1986; Sposito, 1982), numerous modifications of Eq. [1] exist (Grant et al., 1998; Hinz, 2001; Kinniburgh, 1986; Limousin et al., 2007). In this study, we fit two of these modified Langmuir models: the three-parameter Langmuir–Freundlich model and the four-parameter two-surface Langmuir model. The Langmuir–Freundlich model, also known as the exponential Langmuir model, is a power function based on the assumption of continuously distributed affinity coefficients (Sposito, 1980):

$$S = \frac{S_{\max} KC^{\beta}}{1 + KC^{\beta}} \quad [2]$$

where β is a fitting parameter ($0 < \beta < 1$). The two-surface Langmuir model is based on the assumption that sorption occurs on two types of surfaces, each with different bonding energies (Holford et al., 1974):

$$S = \frac{S_{\max_1} K_1 C}{1 + K_1 C} + \frac{S_{\max_2} K_2 C}{1 + K_2 C} \quad [3]$$

where the subscripts refer to the sorption capacity and distribution coefficient for the two different surfaces.

Best-fit, or optimal, model parameters for the nonlinear equations were obtained by finding the combination of parameters that provide the best fit to the observed data. Although numerous statistical packages exist that are capable of fitting nonlinear equations, in this study we developed an easy-to-use Microsoft Excel spreadsheet capable of performing nonlinear weighted least squares regression. The spreadsheet generates best-fit parameters, standard errors of the parameters, 95% confidence intervals of the parameters, parameter correlations, and a goodness-of-fit measure while requiring minimal effort by the user. The spreadsheet was used to fit all nonlinear models to the data. The accuracy of the Excel spreadsheet was assessed by fitting the three nonlinear equations to the sorption data using both the Excel spreadsheet and the more sophisticated statistical software package SAS (SAS Institute, 2003) and comparing parameter estimates, sums-of-squares, parameter uncertainties, and parameter correlations. The SAS PROC NLIN procedure with the Marquardt method was used. A brief description of the spreadsheet and the model-fitting process follows.

Nonlinear Regression

Model parameters are generally estimated by minimizing an objective function. An objective function is a metric that measures the difference between observed and modeled data. Therefore, the goal of the nonlinear data-fitting process is to find the optimal set of parameter values that minimizes the objective function. The spreadsheet presented here uses the method of least squares regression for fitting the nonlinear

equations to the observed data. This method seeks to minimize the sum of the squared errors (SSE) between observed and calculated values of the dependent variable, in this case the sorbed concentration, S :

$$\text{SSE} = \sum_{i=1}^N w_i [S_i - \hat{S}_i]^2 \quad [4]$$

where SSE is the objective function to be minimized, N is the number of observations, w_i is the i th weighting factor (see below), S_i is the i th measured value of the dependent variable, and \hat{S}_i is the i th model-predicted value of the dependent variable.

By including w_i in Eq. [4], the user has the option of using weighted least squares regression. If it is known that the data vary in accuracy, the data can be weighted so that the more accurate data exert a greater influence during model calibration. A common approach is to set the weighting factor for each data point to be the inverse of the measured variance of the data ($w = 1/\sigma^2$). If the variance of the data is unknown, other weighting schemes can be used. One approach is to use relative weighting ($w = 1/S^2$). In this case, the uncertainty in the data is assumed to be proportional to the data themselves. The accuracy of the spreadsheet was tested against SAS using both weighted ($w = 1/S^2$) and unweighted ($w = 1$) data.

Goodness-of-Fit Measure

Numerous methods exist for determining goodness of fit (Kvalseth, 1985); however, only one measure is calculated in the spreadsheet—the model efficiency—because this statistic is considered by many to be the best overall indicator of model fit (Kvalseth, 1985; Mayer and Butler, 1993). The model efficiency, E (Nash and Sutcliffe, 1970), is calculated as

$$E = 1 - \frac{\sum_{i=1}^N w_i (S_i - \hat{S}_i)^2}{\sum_{i=1}^N (w_i S_i - S_{\text{avg}})^2} \quad [5]$$

where S_{avg} is the weighted mean of the measured values and all other variables are as defined above. A model efficiency of 1 indicates a perfect fit to the data, whereas a model efficiency value of <0 indicates that taking the average of all the measured values would give a better prediction than the model. Some statistical packages such as SAS refer to the value calculated in Eq. [5] as r^2 ; however, this is a misnomer because Eq. [5] can result in a negative number and the square of a real number can never be negative.

Parameter Uncertainties

In addition to goodness-of-fit measures, parameter uncertainties are a useful metric when assessing the ability of a model to describe a data set. (Poor model fits tend to produce large parameter uncertainties, whereas good model fits tend to produce small parameter uncertainties.) The uncertainty in the fitted parameter values can be determined from the Jacobian matrix, \mathbf{J} :

$$\mathbf{J} = \begin{bmatrix} \frac{\partial S_1}{\partial b_1} & \frac{\partial S_1}{\partial b_2} & \dots & \frac{\partial S_1}{\partial b_p} \\ \frac{\partial S_2}{\partial b_1} & \frac{\partial S_2}{\partial b_2} & \dots & \frac{\partial S_2}{\partial b_p} \\ \vdots & \vdots & & \vdots \\ \frac{\partial S_N}{\partial b_1} & \frac{\partial S_N}{\partial b_2} & \dots & \frac{\partial S_N}{\partial b_p} \end{bmatrix} \quad [6]$$

where b is the best-fit parameter value, p is the number of fitting parameters, and all other variables are as defined above. The Jacobian matrix can be approximated by the perturbation method using finite differences (Becker and Yeh, 1972):

$$\frac{\partial S_i}{\partial b_i} \approx \frac{S_i(b_i + \Delta b) - S_i(b_i)}{\Delta b_i} \quad [7]$$

where Δb is the amount by which each parameter is perturbed ($0.01b$), $S(b)$ are the predicted values using the best-fit parameter values, and $S(b + \Delta b)$ are the predicted values using the perturbed parameter values.

Assuming that the fitted parameters represent the true global minimum of the objective function, the parameter uncertainties can be approximated from the covariance matrix. The covariance matrix, **Cov**, is calculated from the Jacobian matrix by (Draper and Smith, 1981):

$$\mathbf{Cov} = \left(\frac{\text{SSE}}{n - p} \right) \mathbf{A}^{-1} \quad [8]$$

where **A** is defined as

$$\mathbf{A} = \mathbf{J}^T \mathbf{J} = \begin{bmatrix} \sum_{i=1}^N w_i \left(\frac{\partial S_i}{\partial b_1} \frac{\partial S_i}{\partial b_1} \right) & \cdots & \sum_{i=1}^N w_i \left(\frac{\partial S_i}{\partial b_1} \frac{\partial S_i}{\partial b_p} \right) \\ \vdots & \ddots & \vdots \\ \sum_{i=1}^N w_i \left(\frac{\partial S_i}{\partial b_p} \frac{\partial S_i}{\partial b_1} \right) & \cdots & \sum_{i=1}^N w_i \left(\frac{\partial S_i}{\partial b_p} \frac{\partial S_i}{\partial b_p} \right) \end{bmatrix} \quad [9]$$

To obtain \mathbf{A}^{-1} , we used the MINVERSE function in Excel.

The standard error (SE) of each parameter is given by the square root of the main diagonal of the covariance matrix (Eq. [8]). From the standard errors, the 95% confidence intervals for the fitted parameters (b) can be approximated by

$$b_{\min} = b_{\text{fit}} - t_{0.05, N-p} \text{SE} \quad [10]$$

$$b_{\max} = b_{\text{fit}} + t_{0.05, N-p} \text{SE} \quad [11]$$

where $t_{0.05, N-p}$ is the value of the t distribution for a 95% probability level for a two-tailed test and $N - p$ degrees of freedom. (The appropriate t value is obtained from the TINV function in Excel.) It should be noted that, while the use of confidence intervals is common, this method is strictly valid only for cases with one fitting parameter. For cases where more than one parameter is obtained, joint confidence regions are more appropriate, as this method reflects the joint variability between the parameters. See Bolster et al. (2001) and Smith et al. (1998) for examples of how to calculate joint confidence regions.

Parameter Correlations

The correlation between fitted parameters is another useful metric for assessing the ability of a model to describe a data set. For cases where parameters are highly correlated, the fitted parameter values may not be unique. Parameter correlations can be obtained from the correlation matrix, α , which is calculated from the covariance matrix by

$$\alpha_{ij} = \frac{\mathbf{Cov}_{ij}}{(\mathbf{Cov}_{ii})^{1/2} (\mathbf{Cov}_{jj})^{1/2}} \quad [12]$$

where the diagonal of the correlation matrix is filled with 1s, reflecting that each parameter is perfectly correlated with itself. The off-diagonal

reflect the colinearity between the fitted parameters. Values near 1 reflect interdependent parameter estimates, whereas low values on the off-diagonals reflect independent parameter estimates.

Model Comparison

When comparing models with different numbers of fitting parameters, one cannot simply choose the model with the highest goodness-of-fit measure or the lowest SSE as the model that best describes the data. This is because models with more fitting parameters will almost always result in a better overall fit (i.e., reduced SSE and increased E values). Rather, one must determine if the improvement in fit is statistically significant—i.e., does the improvement in fit justify the additional parameters? Two statistical approaches are commonly used for comparing models with different numbers of fitting parameters: the extra sum of squares principle and Akaike's Information Criterion.

For comparing nested models—that is, models in which one is a generalization or specialization of the other—the extra sum of squares principle can be applied. In this approach, an F ratio is calculated from the differences in the SSEs between the two models (Draper and Smith, 1981):

$$F = \frac{(\text{SSE}_1 - \text{SSE}_2) / (p_2 - p_1)}{\text{SSE}_2 / (N - p_2)} \quad [13]$$

where the subscript 1 represents the simpler model (Model 1) and subscript 2 represents the model with the greater number of fitting parameters (Model 2). A P value is determined from the F ratio by the FDIST command in Excel. If the P value is below the chosen significance level, then the alternative model (Model 2) fits the data significantly better than the null hypothesis model (Model 1).

In contrast to the extra sum of squares principle, which is based on hypothesis testing, Akaike's Information Criterion (AIC) is based on information theory and can be used for both nested and nonnested models. When N is small compared with p , as is usually the case for sorption isotherms, the corrected AIC should be used (Burnham and Anderson, 2002):

$$\text{AIC} = N \ln \left(\frac{\text{SSE}}{N} \right) + 2(p+1) + \frac{2(p+1)(p+2)}{N - p - 2} \quad [14]$$

The model with the lowest AIC is considered to be the most likely to be correct. The probability that the model with the lowest AIC score is the correct model can be calculated by

$$P = \frac{\exp(0.5\Delta)}{1 + \exp(0.5\Delta)} \quad [15]$$

where Δ is the absolute difference in AIC between the two models. It should be noted that Eq. [14] is only valid when the number of data points exceeds the number of fitting parameters by three or more, although it is recommended that the number of data points exceed the number of fitting parameters by five or more to ensure that the reduction in SSE required to accept the higher parameter model is reasonable (Fig. 1). It should also be noted that the extra sum of squares principle and AIC are only valid for comparing models fit on exactly the same data and using the same weighting scheme. These methods are not appropriate for comparing model fits using different weighting schemes or different ways of expressing the dependent variable (such as comparing Eq. [1] with linearized versions of Eq. [1]).

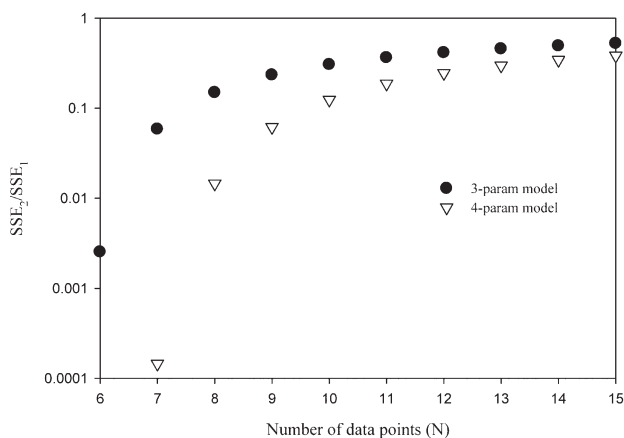


Fig. 1. Relationship between number of data points and reduction in the sum of squared errors (SSE) required to obtain a 95% probability that a three- or four-parameter model is superior to a two-parameter model using Akaike's Information Criterion (AIC). For example, for seven data points, nearly a four order-of-magnitude reduction in SSE is required to obtain a 95% probability that the fit provided by a four-parameter model is superior to the fit provided by a two-parameter model. On the other hand, for 10 data points, the required reduction in SSE is less than one order of magnitude.

RESULTS

Spreadsheet Validation

The layout of the spreadsheet is shown in Fig. 2. The equilibrium (milligrams per liter) and sorbed (milligrams per kilogram) concentrations are entered or pasted into Columns A and B, respectively. Weights for each data point are entered in Column D (optional). If Column D is left blank, unweighted least squares (i.e., $w_i = 1$) is used. As written, the spreadsheet can accommodate up to 25 data points but easily can be modified to include more. The spreadsheet uses the Solver Add-In function to perform the nonlinear regression. The maximum run time, maximum number of iterations, precision, tolerance percentage, convergence criteria, and

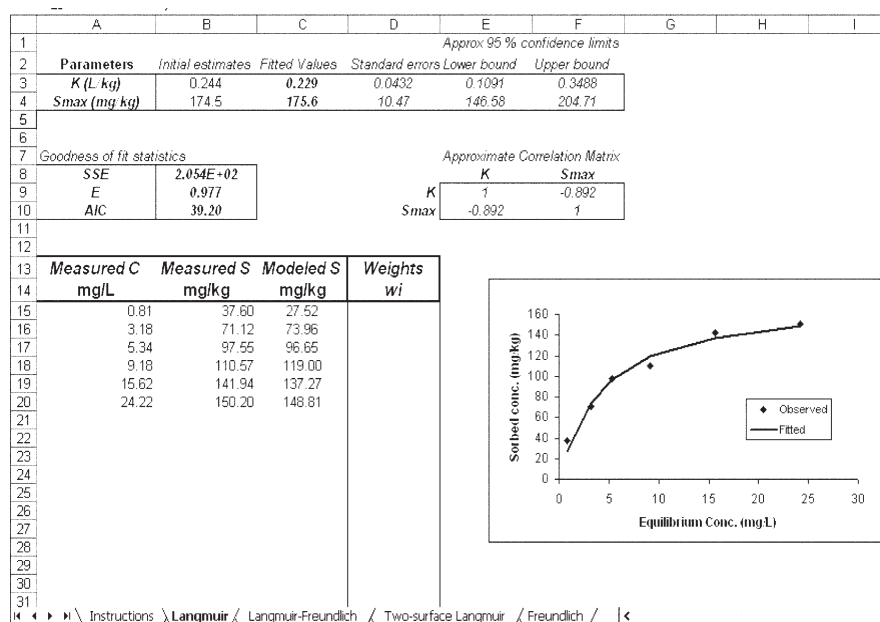


Fig. 2. Example of Excel spreadsheet for fitting nonlinear sorption equations to sorption isotherm data.

search method can all be modified by selecting the Options button in the Solver dialog box. The default settings have been modified as follows: number of iterations = 1×10^4 , precision = 1×10^{-6} , tolerance = 1%, and convergence = 1×10^{-5} . Parameter constraints can be defined in the Solver dialog box. The spreadsheet is written so that the parameters are constrained to ensure positive parameter values. The spreadsheet produces best-fit parameter values, standard errors of the parameters, 95% confidence intervals of the parameters, model efficiency, and the correlation matrix (Fig. 2).

Comparing the fitted parameter values, SSE, standard error of the parameter estimates, and the parameter correlations between the spreadsheet and the SAS PROC NLIN procedure shows that the spreadsheet produces nearly identical results to SAS for all three nonlinear equations tested using both weighted ($w = 1/S^2$) and unweighted ($w = 1$) least squares regression (Fig. 3 and 4). This strong similarity between the two software packages indicates that the more accessible and easily used Excel spreadsheet is accurate and robust enough to obtain good parameter estimates with these nonlinear equations.

Equation Comparisons

To compare model fits between the different linearizations and the nonlinear equation, the best-fit lines for each linearization were transformed back to sorbed concentrations, S , and the SSE and E values were calculated on the untransformed data. Comparing goodness-of-fit measures between the different linearizations and the nonlinear equation shows that the nonlinear equation yielded the lowest SSE and highest E values for all soils (Table 2). With the exception of the Hartsells and Melvin soils, Linearization I yielded the second lowest SSE and second highest E values, followed by Linearizations IV, III, and II. The SSE values for the different linearizations exceeded the SSE values for the nonlinear equation by 7 to 49% for Linearization I, 52 to 309% for Linearization II, 25 to 163% for Linearization III, and 11 to 92% for Linearization IV.

Of the four linearizations tested, Linearization I provided the most similar estimates of S_{\max} and K to the nonlinear equation, followed by Linearizations IV, III, and II (Fig. 5). For all soils, the fitted values for S_{\max} obtained from Linearizations I, III, and IV were all within the 95% confidence intervals of the fitted values obtained by the nonlinear equation. On the other hand, only fitted values of K obtained from Linearization I were within the 95% confidence intervals of the fitted values obtained by the nonlinear equation for all eight soils tested.

For all soils tested, the Langmuir-Freundlich and the two-surface Langmuir models provided better fits to the data than the original Langmuir model, as reflected by a decrease in SSE and an increase in E ; in several cases, the SSE was reduced by

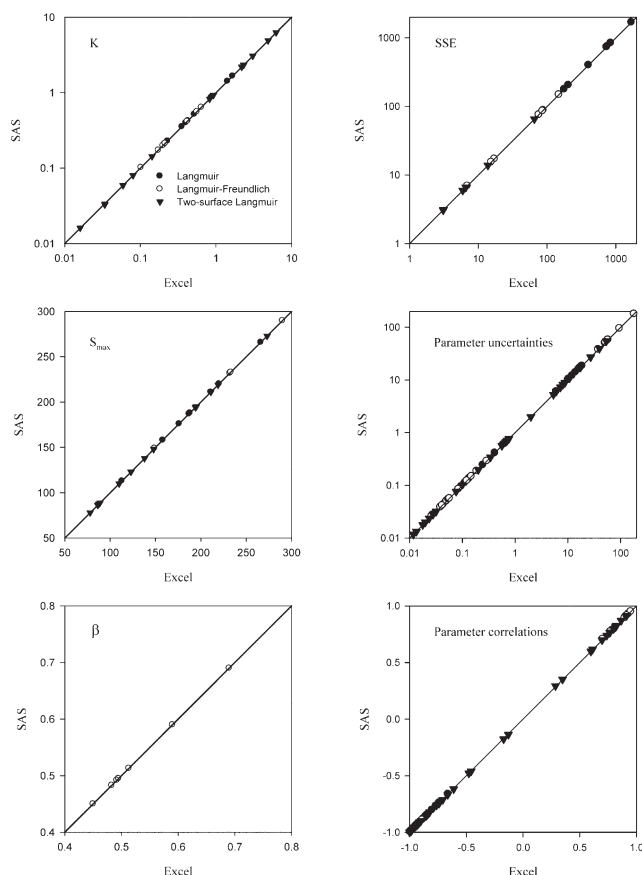


Fig. 3. Comparisons of fitted parameter values and statistics (K is the Langmuir binding-strength coefficient, SSE is the sum of squared errors, S_{\max} is the maximum sorption capacity of the soil, and β is the exponent in the Langmuir–Freundlich model) between SAS and Excel obtained by fitting the Langmuir, Langmuir–Freundlich, and two-surface Langmuir models to sorption data using unweighted nonlinear least squares regression. Parameter values and statistics all fall on the 1:1 line, indicating that the Excel spreadsheet yields nearly identical values as SAS.

more than an order of magnitude (Table 3). Using the extra sum of squares principle, both the Langmuir–Freundlich and two-surface Langmuir models provided significantly better fits ($P < 0.05$) than the original Langmuir model for six of the eight soils. There were not enough data points to use the AIC to perform a statistical comparison between the Langmuir–Freundlich and two-surface Langmuir models.

The differences in fit obtained with the different models are shown in Fig. 6 for three of the soils. For the Collins soil (Fig. 6a), the Langmuir model underpredicted the measured sorbed concentrations at both low and high concentration values. The two modified versions of the Langmuir equation, on the other hand, captured both low and high concentrations quite well and, based on the sum of squares principle, both equations provided fits that were statistically superior ($P < 0.05$) to the original Langmuir equation. For the Loring soil (Fig. 6b), the original Langmuir equation again underpredicted both low and high concentrations, whereas the two modified equations predicted all concentrations quite well, with both modified Langmuir models providing statistically superior fits to the original Langmuir model at the $P = 0.05$ level. For the Pembroke soil (Fig. 6c), although the two modified Langmuir mod-

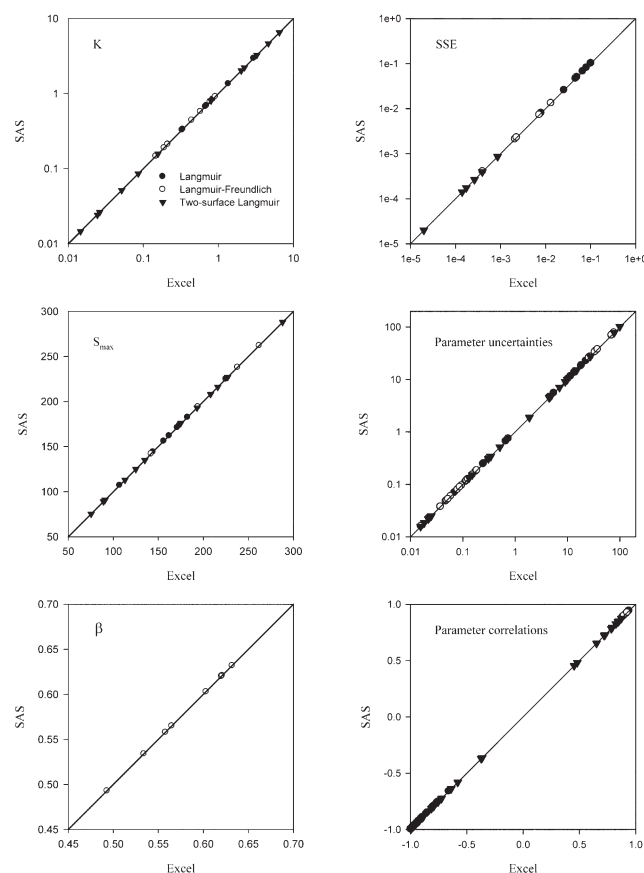


Fig. 4. Comparisons of fitted parameter values and statistics (K is the Langmuir binding-strength coefficient, SSE is the sum of squared errors, S_{\max} is the maximum sorption capacity of the soil, and β is the exponent in the Langmuir–Freundlich model) between SAS and Excel obtained by fitting the Langmuir, Langmuir–Freundlich, and two-surface Langmuir models to sorption data using weighted ($w = 1/S^2$, where w is the weighting factor and S is the measured value) nonlinear least squares regression. Parameter values and statistics all fall on the 1:1 line, indicating that the Excel spreadsheet yields nearly identical values as SAS.

els both predicted the lowest concentration better than the original Langmuir model, the improvements in fit were not considered statistically significant ($P > 0.05$).

DISCUSSION

Of the four linearizations tested in our study, Linearization I—the linearized form most commonly used in P sorption studies—provided fits to the data most similar to the nonlinear equation. Indeed, estimates of both S_{\max} and K obtained with Linearization I were within the 95% confidence level of the parameter estimates obtained with the nonlinear equation for all eight soils tested. This is consistent with the findings of others, who have reported obtaining similar parameter values from the nonlinear Langmuir equation and Linearization I (Fang et al., 2005; Geringa et al., 1995; Kumar and Sivanesan, 2005). Also consistent with other studies is our observation that Linearization II generally provided the poorest fits (i.e., highest SSE values) and most dissimilar parameter estimates to the nonlinear equation of all the linearizations (Colquhoun, 1969, 1971; Dowd and Riggs, 1965; Harrison and Katti, 1990; Harter, 1984).

Table 2. Model efficiency (*E*) and sum of squared errors (SSE) for the nonlinear and linearized Langmuir equations for eight different soils.

Soil series	Nonlinear Langmuir		Linearization I		Linearization II		Linearization III		Linearization IV	
	SSE	<i>E</i>	SSE	<i>E</i>	SSE	<i>E</i>	SSE	<i>E</i>	SSE	<i>E</i>
Belknap	737	0.958	813	0.954	2749	0.844	1734	0.901	1306	0.926
Collins	750	0.954	823	0.950	3045	0.815	1975	0.880	1438	0.913
Hartsells	845	0.921	1258	0.882	1456	0.863	1198	0.887	1045	0.902
Lakin	401	0.964	431	0.961	1249	0.887	779	0.929	599	0.946
Loring	735	0.949	917	0.936	1457	0.899	1087	0.925	937	0.935
Melvin	178	0.949	218	0.937	270	0.922	223	0.936	197	0.943
Pembroke	205	0.977	220	0.976	833	0.909	484	0.947	351	0.962
Zanesville	1689	0.952	1960	0.945	6146	0.826	3746	0.894	2913	0.918

While differences between linear and nonlinear forms of the Langmuir model have been discussed in the literature for several decades (Colquhoun, 1969, 1971; Dowd and Riggs, 1965; Kinniburgh, 1986; Kumar and Sivanesan, 2005; Schulthess and Dey, 1996), much of this work has been conducted on simulated data sets where measurement error was assigned only to the

dependent variable and the independent variable was assumed to be error free (Atkins and Nimmo, 1975; Colquhoun, 1969; Dowd and Riggs, 1965; Harrison and Katti, 1990; Hounsg and Lee, 1998; Persoff and Thomas, 1988). In cases where the dependent variable is directly measured and the independent variable is directly controlled by the experimenter, such as is the case with

the application of the Michaelis–Menten equation to enzyme kinetics, the assumption of an error-free independent variable may be valid. For sorption studies, however, this is not the case because the dependent variable (sorbed concentration) is usually determined from the difference between initial concentrations (the true independent variable) and measurements of the so-called independent variable (equilibrium concentration). Therefore, the assumption of the so-called independent variable being error free is not representative of actual sorption studies. Another limitation to these earlier studies is that the simulated data were generated using only two types of error structure: constant error variance and error variance increasing linearly with the independent variable (i.e., constant relative error). Yet it is unclear whether either of these two error structures are representative of actual sorption studies. Finally, even in studies that do compare fitted parameter values using measured sorption data, parameter uncertainties are rarely included so statistical comparisons cannot be made (Allen et al., 2004; Altin et al., 1998; Kumar and Sivanesan, 2005; Kinniburgh, 1986; Schulthess and Dey, 1996; Tsai and Juang, 2000). By using actual sorption data and calculating parameter uncertainties for the fitted parameter values, we have shown that Linearization I will

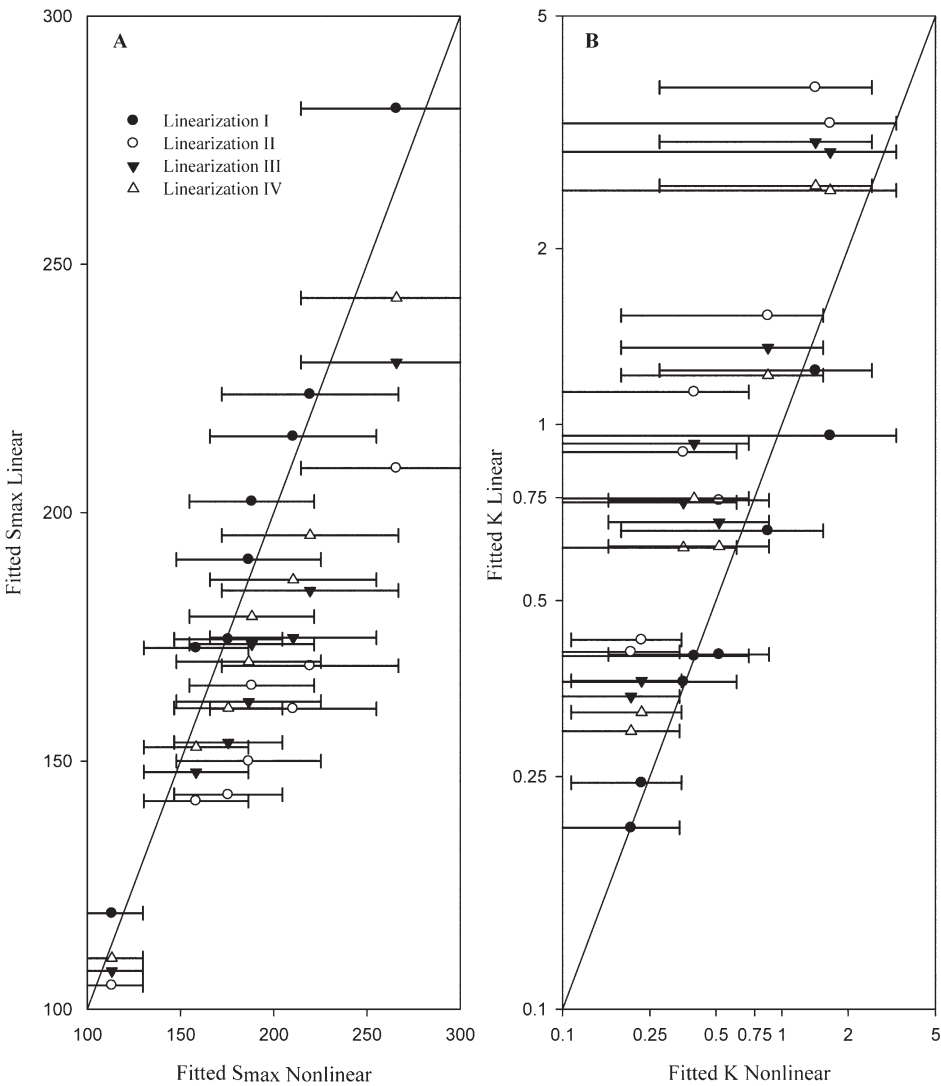


Fig. 5. Comparisons of fitted (A) maximum sorption capacity of the soil (S_{\max}) and (B) Langmuir binding-strength coefficient (K) values between the four linearizations of the Langmuir equation and the nonlinear Langmuir equation. The bars represent the 95% confidence intervals of the fitted parameter values obtained with the nonlinear Langmuir equation.

Table 3. Model efficiency (E) and sum of squared errors (SSE) for the original and modified Langmuir equations for eight different soils. The probability (P) that the modified Langmuir equation provided statistically superior fits than the original Langmuir equation was determined from the extra sum of squares principle (Eq. [13]).

Soil series	Langmuir		Langmuir-Freundlich			Two-surface Langmuir		
	SSE	E	SSE	E	P	SSE	E	P
Belknap	737	0.958	17.2	0.999	0.0015	3.12	>0.999	0.00423
Collins	750	0.954	6.95	>0.999	0.00040	5.94	>0.999	0.00793
Hartsells	845	0.921	149	0.986	0.0333	13.8	0.999	0.0163
Lakin	401	0.964	15.4	0.999	0.0032	0.163	>0.999	0.00041
Loring	735	0.949	76.3	0.995	0.0147	3.08	>0.999	0.00419
Melvin	178	0.949	75.8	0.978	0.138	67.3	0.981	0.379
Pembroke	205	0.977	88.0	0.990	0.139	77.1	0.992	0.375
Zanesville	1689	0.952	86.0	0.998	0.0050	6.59	>0.999	0.00390

generally provide statistically similar parameter estimates as the nonlinear equation for P sorption studies.

In addition to accuracy, an important factor to consider when selecting an equation is whether the equation is sensitive to non-ideality (Schulthess and Dey, 1996). That is, if the sorption data do not conform to the Langmuir model, then the equation should perform poorly so that the Langmuir model can be easily rejected. Erroneously good fits and high E values can be obtained when fitting Linearization I to data not well described by the Langmuir model due to the fact that, in this equation, both x and y axes contain the variable C and therefore are not independent of each other. This lack of independence leads to an artificial trend (Dowd and Riggs, 1965; Harter, 1984), sometimes referred to as *spurious correlation* (Kronmal, 1993), between x and y regardless of the values of S . For example, fitting Linearization I to the transformed sorption data collected on the Hartsells soil resulted in what appeared to be a very good fit to the data, with an E value of 0.994 (Fig. 7a). When using the best-fit parameters from Linearization I in the nonlinear equation, however, the fit does not appear as strong (Fig. 7b). Indeed, the model efficiency decreases to 0.88 when calculated on the untransformed data. When fitting the data with the nonlinear equation, on the other hand, it is much clearer that the data are not fit well by the Langmuir model. Therefore, the primary drawback to Linearization I is not the inability to provide similar parameter estimates as the nonlinear equation but rather the inability to provide poor model fits when the data do not conform to the Langmuir model.

Because linearized Langmuir equations are so easily used, the validity of the Langmuir model is rarely questioned, even though some of the assumptions behind the model have been shown to be violated in solute sorption studies (Elprince and Sposito, 1981; Harter and Baker, 1977, 1978). In fact, many times sorption data do not conform to the Langmuir model (Giles et al., 1974; Grant et al., 1998; Gu et al., 1994), therefore the biggest limitation to relying solely on linear regression to obtain sorption parameters is not the accuracy of the linearized Langmuir equations but rather the inability to test more sophisticated sorption models in describing the data. For instance, although the nonlinear Langmuir equation did provide better fits to our sorption data than did the four linearized versions, these improvements were minor when compared with the improvements obtained with the modified Langmuir equations. Indeed, based on the extra sum of squares principle, the improvement in fit was statistically significant for a majority of the soils tested in our study. This suggests that the Langmuir model was not the best model for describing these data and there-

fore fitted parameter values obtained with this model are probably not representative of these soils. (This is further supported by the large uncertainties in the parameter estimates obtained with the original Langmuir model.)

Using an incorrect sorption model can have significant implications on soil management decisions. For instance, the Langmuir model is often used to estimate the sorption maxima of a soil so that

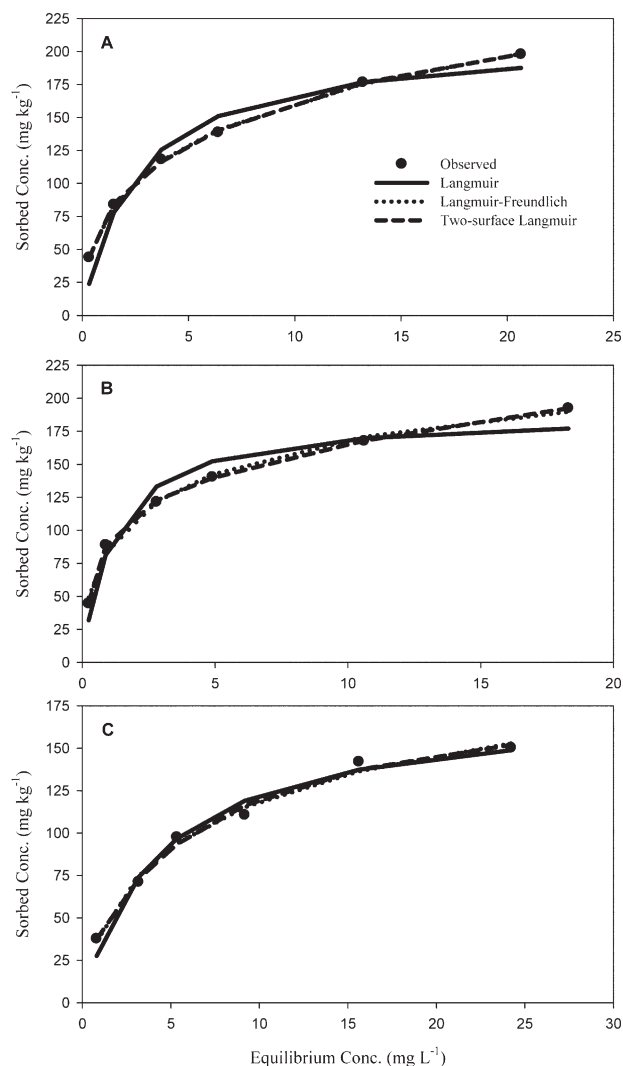


Fig. 6. Measured sorption data and model fits for (A) Collins, (B) Loring, and (C) Pembroke soils.

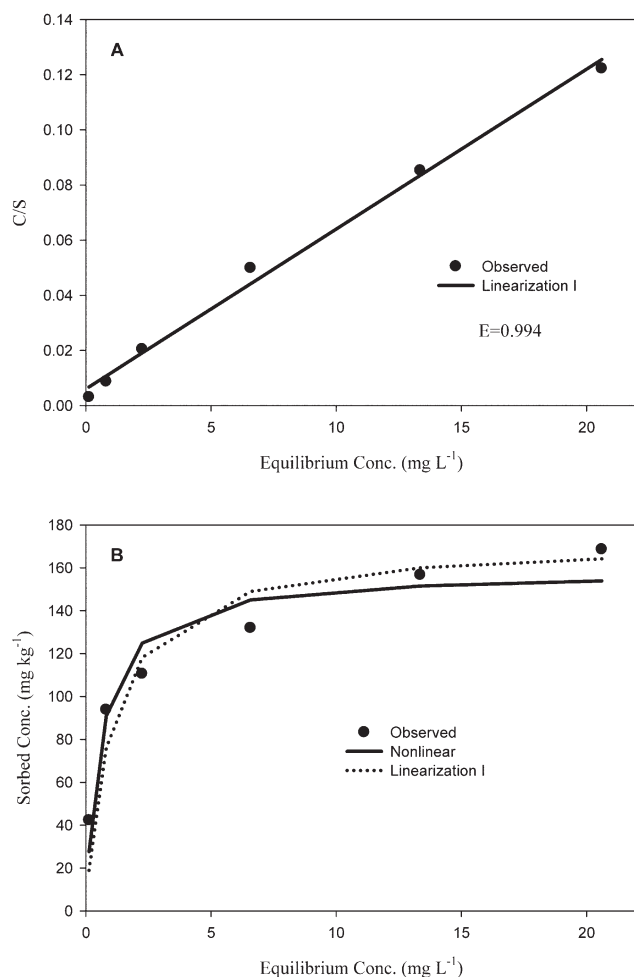


Fig. 7. Model fits to sorption data measured for the Hartsells soil obtained with (A) Linearization I (Table 1) and (B) the nonlinear equation. Also shown in (B) is the model fit obtained with Linearization I but transformed to sorbed concentration.

a P soil saturation index can be calculated (Kleinman and Sharpley, 2002). The soil saturation index is a ratio of sorbed P to P sorption capacity and thereby quantifies the remaining sorption capacity of the soil (Breeuwsma et al., 1995). If the saturation index is high, then the soil is nearing saturation and presumably cannot bind much additional P. In contrast, a soil with a low P saturation index has a greater ability to bind P and therefore little P is expected to be released from the soil (Fang et al., 2002; Pote et al., 1999; Sharpley, 1995). If the data do not conform to the Langmuir model, then fitted S_{\max} values are not representative of the true sorption capacity of the soil and calculating P saturation indices based on these S_{\max} values would be in error, thus potentially leading to ineffective management decisions. It is worth pointing out, however, that even when sorption data do appear to conform to the Langmuir model, fitted S_{\max} values do not necessarily reflect the true sorption capacity of the soil (Harter, 1984; Hough and Lee, 1998).

By including the F test and AIC in the spreadsheet, we give users two statistical measures to help guide which equation is the most suitable for describing the data. A good fit to the data, however, does not mean necessarily that the underlying assumptions of the model are correct or that the fitted parameter values have actual physical meaning (Elprince and Sposito, 1981; Harter and

Baker, 1977, 1978; Olsen and Watanabe, 1957; Veith and Sposito, 1977). For instance, the assumption behind the two-surface model is that sorption occurs on two types of surfaces, each with different bonding energies (Holford et al., 1974), yet Sposito (1982) showed that the two-surface model is capable of fitting data under a much broader range of conditions. Given the numerous modified versions of the Langmuir model that exist, as well as other more sophisticated sorption models not based on the Langmuir model, it is likely that several different models may describe the data equally well, so choosing the correct model will require some understanding of the mechanisms involved (Grant et al., 1998; Hinz, 2001; Kinniburgh, 1986; Limousin et al., 2007). (Guidelines for choosing the correct type of sorption equation are provided by Hinz [2001]). Nevertheless, the ability to test more sophisticated models can help in elucidating the underlying mechanisms controlling sorption and lead to more physically realistic parameter values.

Regardless of the sorption model used, an important assumption of least squares regression analysis is that the uncertainty in the measured values is the same for all measured values. If it is known that the data vary in accuracy, the data can be weighted so that the more accurate data exert a greater influence during model calibration. The use of properly weighted data has been shown, in some cases, to reduce the differences in fitted parameter values between linear and nonlinear versions of the Langmuir equation (Allen et al., 2004; Barry, 1990; Dowd and Riggs, 1965; Kinniburgh, 1986; Mannervik et al., 1986; Persoff and Thomas, 1988; Schulthess and Dey, 1996). Because the use of weighted data will affect model fits and SSE values, statistical comparisons between models may yield different results, depending on whether the data are weighted or unweighted. The difficulty with weighting data, however, is in deciding on the weighting factor to be used. One method is to weight the data by the inverse of the measurement variance. In practice, though, it is unlikely that the true variance will be known due to inadequate replication (Bothwell and Walker, 1995). Alternatively, weighting factors can be based on the data themselves. For instance, if the relative uncertainty of the data is thought to be constant, then the inverse of the square of the data can be used as the weighting factor. Because weighting data with incorrect estimates of the measurement uncertainty can actually result in poorer parameter estimates than if the data remained unweighted (Bothwell and Walker, 1995), weighted least squares regression should only be done if good estimates of the uncertainty in the data are available.

Given the potential problems associated with linearization of nonlinear equations and the availability of nonlinear regression tools, it has been recommended for some time that linear solutions to the Langmuir model be discarded in favor of fitting the nonlinear Langmuir equation to untransformed data (Harrison and Katti, 1990; Kinniburgh, 1986; Persoff and Thomas, 1988). Our findings show that the largest drawback to using linearized Langmuir equations is not necessarily the statistical deficiencies of these linearizations, but rather the inability to test more sophisticated models that may be more appropriate for describing the data. Even though numerous statistical packages exist that are capable of performing nonlinear regression, the continued use of linearized Langmuir equations (Borling et al., 2001; D'Angelo et al., 2003; Fang et al., 2002; Kleinman and Sharpley, 2002; Siddique and Robinson, 2003; Xu et al., 2006) suggests that access to nonlinear regression tools may still be limited. Therefore, by developing an accurate and easy-to-

use spreadsheet capable of fitting nonlinear Langmuir equations to sorption data, our study should encourage a more critical approach to fitting isotherm data as well as offer the flexibility of testing more sophisticated models. Even though the spreadsheet currently includes only two modified versions of the Langmuir model it can easily be modified to include any two-, three- or four-parameter model. (The corresponding author may be contacted if assistance is needed.) The results of this study should allow researchers to make more informed decisions when applying the Langmuir model to their sorption data.

ACKNOWLEDGMENTS

This research was part of USDA-ARS National Program 206: Manure and By-product Utilization. We are grateful for the helpful comments we received on an earlier version of the manuscript from Jason Warren, Debbie Boykin, and Mark Ducey. Mention of trade names or commercial products is solely for the description of experimental procedures and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

REFERENCES

- Allen, S.J., G. McKay, and J.F. Porter. 2004. Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems. *J. Colloid Interface Sci.* 280:322–333.
- Altin, O., H.O. Ozbelge, and T. Dogu. 1998. Use of general purpose adsorption isotherms for heavy metal–clay mineral interactions. *J. Colloid Interface Sci.* 198:130–140.
- Atkins, G.L., and I.A. Nimmo. 1975. A comparison of seven methods for fitting the Michaelis–Menten equation. *Biochem. J.* 149:775–777.
- Barry, D.A. 1990. Comments on “Estimating Michaelis–Menten or Langmuir isotherm constants by weighted nonlinear least squares.” *Soil Sci. Soc. Am. J.* 54:941–942.
- Becker, L., and W.W.-G. Yeh. 1972. Identification of parameters in unsteady open-channel flows. *Water Resour. Res.* 8:956–965.
- Bolster, C.H., A.L. Mills, G.M. Hornberger, and J.S. Herman. 2001. Effect of surface coatings, grain size, and ionic strength on the maximum attainable coverage of bacteria on sand surfaces. *J. Contam. Hydrol.* 50:287–305.
- Borling, K., E. Otabbong, and E. Barberis. 2001. Phosphorus sorption in relation to soil properties in some cultivated Swedish soils. *Nutr. Cycling Agroecosyst.* 59:39–46.
- Bothwell, M.K., and L.P. Walker. 1995. Evaluation of parameter estimation methods for estimating cellulase binding constants. *Bioresour. Technol.* 53:21–29.
- Breeuwsma, A., J.G.A. Reijerink, and O.F. Schoumans. 1995. Impact of manure on accumulation and leaching of phosphate in areas of intensive livestock farming. p. 239–249. *In* K. Steel (ed.) *Animal waste and the land–water interface*. Lewis Publ., Boca Raton, FL.
- Burnham, K.P., and D.R. Anderson. 2002. *Model selection and multimodel inference: A practical information–theoretic approach*. Springer, New York.
- Colquhoun, D. 1969. A comparison of estimators for a two-parameter hyperbola. *J. R. Stat. Soc. Ser. A* 18:130–140.
- Colquhoun, D. 1971. *Lectures on biostatistics*. Clarendon Press, Oxford.
- D’Angelo, E.M., M.V. Vandiviere, W.O. Thom, and F. Sikora. 2003. Estimating soil phosphorus requirements and limits from oxalate extract data. *J. Environ. Qual.* 32:1082–1088.
- Dowd, J.E., and D.S. Riggs. 1965. A comparison of estimates of Michaelis–Menten kinetic constants from various linear transformations. *J. Biol. Chem.* 240:863–869.
- Draper, N.R., and H. Smith. 1981. *Applied regression analysis*. John Wiley & Sons, New York.
- Elprince, A.M., and G. Sposito. 1981. Thermodynamic derivation of equations of the Langmuir type for ion equilibria in soils. *Soil Sci. Soc. Am. J.* 45:277–282.
- Fang, F., P.L. Brezonik, D.J. Mulla, and L.K. Hatch. 2002. Estimating runoff phosphorus losses from calcareous soils in the Minnesota River basin. *J. Environ. Qual.* 31:1918–1929.
- Fang, F., P.L. Brezonik, D.J. Mulla, and L.K. Hatch. 2005. Characterization of soil algal bioavailable phosphorus in the Minnesota River basin. *Soil Sci. Soc. Am. J.* 69:1016–1025.
- Gerringa, L.J.A., P.M.J. Herman, and T.C.W. Poortvliet. 1995. Comparison of the linear Van den Berg/Ruzic transformation and a non-linear fit of the Langmuir isotherm applied to Cu speciation data in the estuarine environment. *Mar. Chem.* 48:131–142.
- Giles, C.H., A.P. D’Silva, and I.A. Easton. 1974. A general treatment and classification of the solute adsorption isotherm: II. Experimental interpretation. *J. Colloid Interface Sci.* 47:766–778.
- Grant, P.G., S.L. Lemke, M.R. Dwyer, and T.D. Phillips. 1998. Modified Langmuir equation for S-shaped and multisite isotherm plots. *Langmuir* 14:4292–4299.
- Gu, B.J., J. Schmitt, Z. Chen, L. Liang, and J.F. McCarthy. 1994. Adsorption and desorption of natural organic matter on iron oxide: Mechanisms and models. *Environ. Sci. Technol.* 28:38–46.
- Harrison, F., and S.K. Katti. 1990. Hazards of linearization of Langmuir’s model. *Chemom. Intell. Lab. Syst.* 9:249–255.
- Harter, R.D. 1984. Curve-fit errors in Langmuir adsorption maxima. *Soil Sci. Soc. Am. J.* 48:749–752.
- Harter, R.D., and D.E. Baker. 1977. Applications and misapplications of the Langmuir equation to soil adsorption phenomena. *Soil Sci. Soc. Am. J.* 41:1077–1080.
- Harter, R.D., and D.E. Baker. 1978. Further reflection on the use of the Langmuir equation in soils research. *Soil Sci. Soc. Am. J.* 42:987–988.
- Hinz, C. 2001. Description of sorption data with isotherm equations. *Geoderma* 99:225–243.
- Holford, I.C.R., R.W.M. Wedderburn, and G.E.G. Mattingly. 1974. A Langmuir two-surface equation as a model for phosphate adsorption to soils. *J. Soil Sci.* 25:242–255.
- Houng, K.-H., and D.-Y. Lee. 1998. Comparisons of linear and nonlinear Langmuir and Freundlich curve-fit in the study of Cu, Cd, and Pb adsorption on Taiwan soils. *Soil Sci.* 163:115–121.
- Kinniburgh, D.G. 1986. General purpose adsorption isotherms. *Environ. Sci. Technol.* 20:895–904.
- Kleinman, P.J.A., and A.N. Sharpley. 2002. Estimating soil phosphorus sorption saturation data from Mehlich-3 data. *Commun. Soil Sci. Plant Anal.* 33:1825–1839.
- Kronmal, R.A. 1993. Spurious correlation and the fallacy of the ratio standard revisited. *J. R. Stat. Soc. Ser. A* 156:379–392.
- Kumar, K.V., and S. Sivanesan. 2005. Prediction of optimum sorption isotherm: Comparison of linear and non-linear method. *J. Hazard. Mater.* B126:198–201.
- Kvalseth, T.O. 1985. Cautionary note about R^2 . *Am. Stat.* 39:279–285.
- Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica, and platinum. *J. Am. Chem. Soc.* 40:1361–1403.
- Limousin, G., J.-P. Gaudet, L. Charlet, S. Szenknect, V. Barthes, and M. Krimissa. 2007. Sorption isotherms: A review on physical bases, modeling and measurement. *Appl. Geochem.* 22:249–275.
- Mannervik, B., I. Jakobson, and M. Warholm. 1986. Error structure as a function of substrate and inhibitor concentration in enzyme kinetic experiments. *Biochem. J.* 235:797–804.
- Mayer, D.G., and D.G. Butler. 1993. Statistical validation. *Ecol. Modell.* 68:21–32.
- Murphy, J., and H.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* 27:31–36.
- Nair, P.S., T.J. Logan, A.N. Sharpley, L.E. Sommers, M.A. Tabatabai, and T.L. Yuan. 1984. Interlaboratory comparison of a standardized phosphorus adsorption procedure. *J. Environ. Qual.* 3:591–595.
- Nash, J.E., and J.V. Sutcliffe. 1970. River flow forecasting through conceptual models. Part 1: A discussion of principles. *J. Hydrol.* 10:282–290.
- Olsen, S.R., and F.S. Watanabe. 1957. A method to determine a phosphorus adsorption maximum of soils as measured by the Langmuir isotherm. *Soil Sci. Soc. Am. Proc.* 21:144–149.
- Persoff, P., and J.F. Thomas. 1988. Estimating Michaelis–Menten or Langmuir isotherm constants by weighted nonlinear least squares. *Soil Sci. Soc. Am. J.* 52:886–889.
- Pote, D.H., T.C. Daniel, D.J. Nichols, A.N. Sharpley, J. Moore, P.A., D.M. Miller, and D.R. Edwards. 1999. Relationship between phosphorus levels in three Ultisols and phosphorus concentrations in runoff. *J. Environ. Qual.* 28:170–175.
- SAS Institute. 2003. *SAS user’s guide: Statistics*. SAS Inst., Cary, NC.
- Schulthess, C.P., and D.K. Dey. 1996. Estimation of Langmuir constants using

- linear and nonlinear least squares regression analyses. *Soil Sci. Soc. Am. J.* 60:433–442.
- Sharpley, A.N. 1995. Dependence of runoff phosphorus on extractable soil phosphorus. *J. Environ. Qual.* 24:920–926.
- Siddique, M.T., and J.S. Robinson. 2003. Phosphorus sorption and availability in soils amended with animal manures and sewage sludge. *J. Environ. Qual.* 32:1114–1121.
- Smith, L.H., P.L. McCarty, and P.K. Kitanidis. 1998. Spreadsheet method for evaluation of biochemical reaction rate coefficients and their uncertainties by weighted nonlinear least-squares analysis of the integrated Monod equation. *Appl. Environ. Microbiol.* 64:2044–2050.
- Sposito, G. 1980. Derivation of the Freundlich equation for ion exchange reactions in soils. *Soil Sci. Soc. Am. J.* 44:652–654.
- Sposito, G. 1982. On the use of the Langmuir equation in the interpretation of “adsorption” phenomena: II. The “two-surface” Langmuir equation. *Soil Sci. Soc. Am. J.* 46:1147–1152.
- Tsai, S.-C., and K.-W. Juang. 2000. Comparison of linear and nonlinear forms of isotherm models for strontium sorption on a sodium bentonite. *J. Radioanal. Nucl. Chem.* 243:741–746.
- Veith, J.A., and G. Sposito. 1977. On the use of the Langmuir equation in the interpretation of “adsorption phenomena.” *Soil Sci. Soc. Am. J.* 41:697–702.
- Wang, J.J., and D.L. Harrell. 2005. Effect of ammonium and sodium cations and phosphate, nitrate, and chloride anions on zinc sorption and lability in selected acid and calcareous soils. *Soil Sci. Soc. Am. J.* 69:1036–1046.
- Xu, D., J. Xu, J. Wu, and A. Muhammad. 2006. Studies on the phosphorus sorption capacity of substrates used in constructed wetland systems. *Chemosphere* 63:344–352.
- Zhang, H., J.L. Schroder, J.K. Fuhrman, N.T. Basta, D.E. Storm, and M.E. Payton. 2005. Path and multiple regression analyses of phosphorus sorption capacity. *Soil Sci. Soc. Am. J.* 69:96–106.